

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of : **BOX PATENT APPLICATION**

Alain FORESTIÈRE et al. : Examiner: Unassigned

Serial No.: Unassigned : Group Art Unit: Unassigned

Filed: August 16, 2001 :

For: MATERIALS COMPRISING ORGANIC PHOSPHOROUS-CONTAINING GROUPS  
BONDED TO A MINERAL OXIDE VIA OXYGEN ATOMS

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, Applicants wish to amend the above-identified application as indicated below:

**IN THE ABSTRACT**

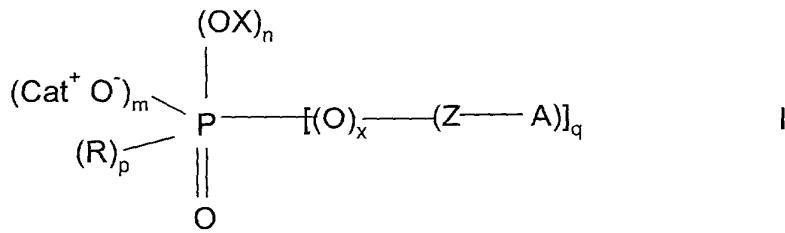
Please delete the existing abstract and replace with the attached Abstract of the Disclosure.

**IN THE CLAIMS**

Please cancel claims 3-9 and 12-15 without prejudice or disclaimer.

Please amend claim 10 as follows:

10. (Amended) A process for preparing a functionalized material according to claim 1, comprising contacting a suspension in a liquid of at least one mineral oxide of an element M with at least one solution in a solvent of at least one phosphorous-containing compound with formula I:



in which the sum  $m+n+p+q$  is equal to 3,  $m=0, 1$  or  $2$ ,  $q=0, 1$  or  $2$ ,  $x=0$  or  $1$ ,  $p=0, 1$  or  $2$ ,  $R$  is a hydrocarbon group,  $X$  is a hydrogen atom, a hydrocarbon group or a group with formula  $SiR''_3$ , in which  $R''$  is a hydrocarbon group,  $Z$  is a hydrocarbon group optionally containing heteroatoms,  $Cat^+$  is a monovalent cation and  $A$  is a sulphur-containing group or a reactive group that can be transformed into a sulphur-containing group, said contact being made under conditions of pressure, temperature and acidity of the medium such that practically no phosphate, phosphonate, phosphinate or sulphate phase of said element M is formed.

Please add the following new claims:

— 16. Functionalized materials according to claim 2, comprising an organic sulphur-containing group selected from the group formed by thiols and derivatives thereof, said sulphonic acid groups and derivatives thereof.

17. Materials according to claim 16, in which the organic sulphur-containing group is selected from the group consisting of a thiol group with formula  $-SH$ , a sulphide group with formula  $-S-R1$  in which  $R1$  is a hydrocarbon residue, and a polysulphide group with formula  $-(S)_y-R1$ , in which  $y$  is a number equal to 2 or more and  $R1$  is a hydrocarbon residue.

18. Materials according to claim 16, in which the organic sulphur-containing group is selected from the group consisting of a sulphonic acid group with formula  $-SO_3H$ , organic sulphonate groups with formulae  $-SO_3R1$  in which  $R1$  is a hydrocarbon residue, and a mineral sulphonate group with formulae  $-SO_3(M')_t$  in which  $M'$  is an element with valency  $t$  from the periodic table.

19. Materials according to claim 18, wherein said organic sulphur-containing group is said mineral sulphonate group of the formulae -  $\text{SO}_3(\text{M}')_{l_t}$  wherein M' is an alkali metal.

20. Materials according to claim 2, comprising a hydrocarbon chain of 1-24 carbon atoms bonding the phosphorous-containing group to the sulphur-containing group.

21. Materials according to claim 20, wherein the hydrocarbon chain bonding the phosphorous-containing group to the sulphur-containing group is an aromatic chain, an aliphatic chain, or a saturated aliphatic chain.

22. Materials according to claim 1, in which M designates an element from groups IB, IIB, IIIB, IVB, VB, VIB, VIIIB, VIII, IIIA, IVA, the lanthanides or the actinides of the periodic table.

23. Materials according to claim 1, in which M is selected from the group consisting of titanium, zirconium, iron, aluminium, silicon and tin.

24. Materials according to claim 23, wherein M is titanium, zirconium or aluminium.

25. A process according to claim 10, in which the phosphorous-containing compound with formula I is a compound in which Z is a saturated divalent alkyl group containing 1 to 6 carbon atoms.

26. A process according to claim 10, in which the solvent for the phosphorous-containing compound is selected from the group consisting of tetrahydrofuran, dimethylsulphoxide, dichloromethane and water.

27. A process according to claim 10, in which the phosphorous-containing compound with formula I is a compound in which m=2, q=1 and n=p=zero.

28. A process according to claim 10, in which the phosphorous-containing compound with formula I employed is a compound in which n=2, q=1 and m=p=zero. -

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**REMARKS**

A principal purpose of this Preliminary Amendment is to facilitate examination and avoid fees for multiply dependent claims, Applicants reserving the right to reintroduce claims to cancelled combined subject matter. New claims 16-19 substantively correspond to claims 3-5; 20-24 to 6-8 and 25-28 to 12-15.

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned "**Version With Markings To Show Changes Made**".

Respectfully submitted,



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## ABSTRACT OF THE DISCLOSURE

Essentially amorphous functionalized materials comprise an essentially monomolecular layer of organic phosphorous-containing groups bonded to a mineral oxide of an element M via an oxygen atom of said oxide to a phosphorous atom that is itself preferably bonded to a hydrocarbon chain substituted at a distance from the phosphorous atom by a sulphur-containing group or by a reactive group that can be transformed into a sulphur-containing group, said materials being essentially free of phosphate, phosphonate and phosphinate phases of said element M and the sulphate of said element M when the materials comprise a sulphur-containing group. A process for preparing functionalized materials brings a suspension in a liquid of at least one mineral oxide of at least one element M into contact with a solution in a solvent of at least one phosphorous-containing compound usually comprising, at a distance from the phosphorous atom, a sulphur-containing group connected to said phosphorous atom via a hydrocarbon chain.

**Version With Markings To Show Changes Made**

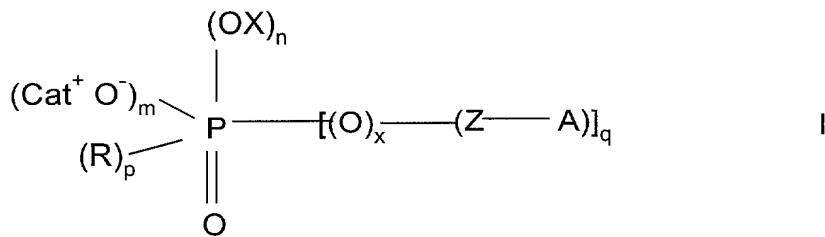
**IN THE ABSTRACT**

The abstract has been replaced with the attached Abstract of the Disclosure, therefore no marked-up version is necessary.

**IN THE CLAIMS**

Claim 10 has been amended as follows:

10. (Amended) A process for preparing a functionalized material according to ~~any one of claims 1 to 9, in which claim 1, comprising contacting~~ a suspension in a liquid of at least one mineral oxide of an element M is brought into contact with at least one solution in a solvent of at least one phosphorous-containing compound with formula I:



in which the sum  $m+n+p+q$  is equal to 3,  $m=0, 1$  or  $2$ ,  $q=0, 1$  or  $2$ ,  $x=0$  or  $1$ ,  $p=0, 1$  or  $2$ , R is a hydrocarbon group, X is a hydrogen atom, a hydrocarbon group or a group with formula  $SiR''_3$ , in which  $R''$  is a hydrocarbon group, Z is a hydrocarbon group optionally containing heteroatoms,  $Cat^+$  is a monovalent cation and A is a sulphur-containing group or a reactive group that can be transformed into a sulphur-containing group, said contact being made under conditions of pressure, temperature and acidity of the medium such that practically no phosphate, phosphonate, phosphinate or sulphate phase of said element M is formed.

Claims 3-9 and 12-15 have been cancelled.